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(54) Title: ANTIFOULING COATING COMPOSITION COMPRISING A FLUORINATED RESIN

(57) Abstract: A process for inhibiting the fouling of a substrate in a marine fouling environment, which comprises forming on the substrate, before exposure to the said environment, a coating comprising a curable fluorinated resin of the general formula: W - L - YFC - O - R<sup>f</sup> - CFY - L - W wherein : W is a group of the general formula -Si(R<sup>1</sup>)<sub>α</sub>(OR<sup>2</sup>)<sub>3-α</sub>, wherein α = 0, 1, or 2, preferably α = 0, R<sup>1</sup> and R<sup>2</sup> independently have the meaning of linear or branched C<sub>1</sub>-C<sub>6</sub> alkyl groups, optionally containing one or more ether groups, or C<sub>7</sub>-C<sub>12</sub> aryl or alkyl groups, and preferably R<sup>1</sup> and R<sup>2</sup> are C<sub>1</sub>-C<sub>4</sub> alkyl groups; L is an organic linking group; Y is F or CF<sub>3</sub>; and R<sup>f</sup> is a group having an average molecular weight by number between 350 and 8000, preferably between 500 and 3000, and comprising repeating units having at least one of the following structures randomly distributed along the chain: -CFXO-, CF<sub>2</sub>CF<sub>2</sub>O-, CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-, CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-, CR<sup>4</sup>R<sup>5</sup>CF<sub>2</sub>CF<sub>2</sub>O-, -(CF(CF<sub>3</sub>)CF<sub>2</sub>O)-, -CF<sub>2</sub>CF(CF<sub>3</sub>)O-, wherein X is F or CF<sub>3</sub>, R<sup>4</sup> and R<sup>5</sup> independently have the meaning of H, Cl, or C<sub>1</sub>-C<sub>4</sub> perfluoroalkyl.

## ANTIFOULING COATING COMPOSITION COMPRISING A FLUORINATED RESIN

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The present invention pertains to a fluorinated resin and the use thereof in antifouling coating compositions for marine applications.

Man-made structures such as boat hulls, buoys, drilling platforms, oil production  
10 rigs, and pipes which are immersed in water are prone to fouling by aquatic organisms such as green and brown algae, barnacles, mussels, and the like. Such structures are commonly of metal, but may also comprise other structural materials such as concrete. This fouling is a nuisance on boat hulls, because it increases frictional resistance during movement through the water, the  
15 consequence being reduced speeds and increased fuel costs. It is a nuisance on static structures such as the legs of drilling platforms and oil production rigs, firstly because the resistance of thick layers of fouling to waves and currents can cause unpredictable and potentially dangerous stresses in the structure, and, secondly, because fouling makes it difficult to inspect the structure for  
20 defects such as stress cracking and corrosion. It is a nuisance in pipes such as cooling water intakes and outlets, because the effective cross-sectional area is reduced by fouling, with the consequence that flow rates are reduced.

The commercially most successful methods of inhibiting fouling have involved the use of anti-fouling coatings containing substances toxic to aquatic life, for  
25 example tributyltin chloride or cuprous oxide. Such coatings, however, are being regarded with increasing disfavour because of the damaging effects such toxins may have if released into the aquatic environment. There is accordingly a need for non-fouling coatings which do not contain markedly toxic materials.

30 It has been known for many years, for example as disclosed in GB 1,307,001 and US 3,702,778 that silicone rubber coatings resist fouling by aquatic organisms. It is believed that such coatings present a surface to which the organisms cannot easily adhere, and they can accordingly be called non-fouling

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rather than anti-fouling coatings. Silicone rubbers and silicone compounds generally have very low toxic properties. Silicone rubber coatings have, however, gained little commercial acceptance. It is difficult to make them adhere well to the substrate surface that is to be protected, and mechanically  
5 they are rather weak and liable to damage.

It is known to use fluorinated polymers for fouling control in anti-fouling or non-fouling coating compositions.

In JP 04-045170 a fluorinated silicone resin is disclosed which is obtained by  
10 grafting a fluorine-containing acrylate to a silicone resin having olefinically unsaturated bonds in its terminal groups.

In JP 61-043668 a coating composition having antifouling properties is disclosed which is prepared by compounding an alkyd resin with a polymer prepared by reacting a fluorine-containing monomer with an acrylate polymer.

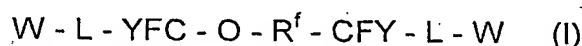
15 In JP 06-322294 a corrosion protecting antifouling coating is disclosed comprising a film forming resin and an organopolysiloxane having oxyalkylene groups and perfluoroalkyl groups.

Fluorinated polymers are also known for other uses.

20 In JP 06-239876 a fluorinated polymer having excellent wetting properties is disclosed that is used in an adhesive. In US 4,900,474 a perfluoroether group-containing organopolysiloxane is disclosed that is used as a silicone antifoamer.

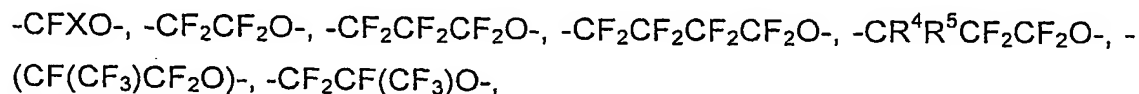
25 None of the fluorinated polymers that are known in the art have found wide application in antifouling coating compositions, since their anti-fouling/foul release properties are not sufficient and/or their mechanical properties do not make these compositions suited for use on various kind of structures that are immersed in water. In particular, the mechanical properties should be such that  
30 if applied as a coating composition for a boat hull, said coating composition should have sufficient strength and abrasion resistance to have a service life of several years.

The object of the present invention is to provide a new antifouling coating composition with very good anti-fouling/foul release properties and sufficient mechanical strength and a process for inhibiting the fouling of a substrate in a marine fouling environment wherein this new antifouling coating composition is used. This process comprises forming on a substrate, before exposure of the substrate to a marine fouling environment, a coating comprising a curable fluorinated resin of the general formula:



wherein

- L is an organic linking group;
- Y is F or CF<sub>3</sub>;
- W is a group of general formula -Si(R<sup>1</sup>)<sub>α</sub>(OR<sup>2</sup>)<sub>3-α</sub>, wherein α = 0, 1, or 2, preferably α = 0, R<sup>1</sup> and R<sup>2</sup> independently have the meaning of linear or branched C1-C6 alkyl groups, optionally containing one or more ether groups, or C7-C12 aryl or alkyl groups, and preferably R<sup>1</sup> and R<sup>2</sup> are C1-C4 alkyl groups;
- R<sup>f</sup> is a group having an average molecular weight by number between 350 and 8000, preferably between 500 and 3000, and comprising repeating units having at least one of the following structures randomly distributed along the chain:



wherein

- X is F or CF<sub>3</sub>,
- R<sup>4</sup> and R<sup>5</sup> independently have the meaning of H, Cl, or C1-C4 perfluoroalkyl.

L preferably is a divalent linking group, more preferably selected from one or more of the following:

- a) -(CH<sub>2</sub>-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>)<sub>m</sub>-CO-NR<sup>1</sup>-(CH<sub>2</sub>)<sub>q</sub>,

wherein

R' is H, C<sub>1</sub>-C<sub>4</sub> alkyl or a phenyl group;

m is an integer equal to 0 or 1, preferably 1;

n is an integer in the range 0-8, preferably 0-5;

q is an integer in the range 1-8, preferably 1-3;

5 b) -CH<sub>2</sub>O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-

c) -CH<sub>2</sub>O-CH<sub>2</sub>-CH(OH)CH<sub>2</sub>-S-(CH<sub>2</sub>)<sub>q</sub>

L can also be a trivalent group. In this case in formula (I) -L-W becomes -L-(W)<sub>2</sub>.

Preference is given to a compound wherein L is A) with m = 1, n = 0-5, and q =  
10 1-3.

Further preference is given to R' being selected from one of the following structures:

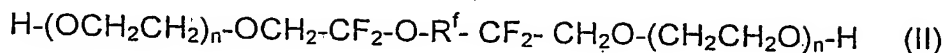
- 1) -(CF<sub>2</sub>O)<sub>a</sub>-(C<sub>2</sub>F<sub>4</sub>O)<sub>b</sub>-, wherein a'/b' is between 0,2 and 2, a' and b' being integers giving the above molecular weight;
- 15 2) -(C<sub>3</sub>F<sub>6</sub>O)<sub>r</sub>-(C<sub>2</sub>F<sub>4</sub>O)<sub>b</sub>-(CFXO)<sub>t</sub>-, wherein r/b is between 0,5 and 2 and (r+b)/t is between 10 and 30, b, r, and t being integers giving the above molecular weight;
- 3) -(C<sub>3</sub>F<sub>6</sub>O)<sub>r</sub>-(CFXO)<sub>t</sub>-CF<sub>2</sub>(R'<sup>f</sup>)<sub>y</sub>-CF<sub>2</sub>O-(CFXO)<sub>t</sub>-(C<sub>3</sub>F<sub>6</sub>O)<sub>r</sub>-, wherein t' is larger than 0, r'/t' is between 10 and 30, r' and t' being integers giving the above  
20 molecular weight, y is 0 or 1, and R'<sup>f</sup> is a C1-C4 fluoroalkyl group;
- 4) -(C<sub>3</sub>F<sub>6</sub>O)<sub>z</sub>-CF<sub>2</sub>-(R'<sup>f</sup>)<sub>y</sub>-CF<sub>2</sub>O-(C<sub>3</sub>F<sub>6</sub>O)<sub>z</sub>-, wherein z is an integer giving the above molecular weight, y is 0 or 1, and R'<sup>f</sup> is a C1-C4 fluoroalkyl group;
- 5) -(OCF<sub>2</sub>CF<sub>2</sub>CR<sup>4</sup>R<sup>5</sup>)<sub>q</sub>-OCF<sub>2</sub>-(R'<sup>f</sup>)<sub>y</sub>-CF<sub>2</sub>O-(CR<sup>4</sup>R<sup>5</sup>CF<sub>2</sub>CF<sub>2</sub>O)<sub>s</sub>-, wherein q and s are integers giving the above molecular weight, R<sup>4</sup> and R<sup>5</sup> have the  
25 meaning given above, y is 0 or 1, and R'<sup>f</sup> is a C1-C4 fluoroalkyl group.

In the above structures -(C<sub>3</sub>F<sub>6</sub>O)- can be -(CF(CF<sub>3</sub>)CF<sub>2</sub>O)- or -(CF<sub>2</sub>CF(CF<sub>3</sub>)O)-.

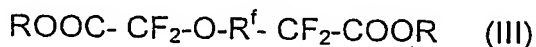
The product of formula (I) can be prepared by the method disclosed in US 4,746,550.

- 30 Good results in foul release and/or mechanical strength were found for a coating composition comprising the fluorinated resin of formula (I) that is obtainable by reacting a silicon compound, as defined below, with bifunctional

perfluoropolyethers having -OH or -COOR end groups, with R=H or C1-C3 of the general formula:

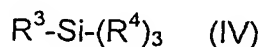


or



wherein  $\text{R}^f$  and  $n$  have the meaning as defined before. These compounds are commercially available from Ausimont under the names Fomblin<sup>®</sup> ZDOL, ZDEAL, ZDOL-TX. However, it is also possible to use bifunctional perfluoroethers having other end groups, e.g., epoxy groups

Examples of suitable silicon compounds which can be reacted with the above bifunctional perfluoropolyether precursors are compounds of the general formula



wherein  $\text{R}^3$  is a group capable of coupling the silicon compound to the fluorinated polyether and the  $\text{R}^4$  groups each independently have the meaning of an ether or ester group, preferably a group including a straight-chain or branched alkyl moiety having from 1 to 4 carbon atoms.

For example, a silicon compound in which  $\text{R}^3$  is an isocyanate-functional group can be coupled to a fluorinated polyether having at least two functional groups selected from hydroxyl, amine, or carboxylic acid-functional groups. A silicon compound in which  $\text{R}^3$  is an amine-functional group can be coupled to a fluorinated polyether having at least two functional groups selected from carboxylic acid ester or epoxy-functional groups. A silicon compound in which  $\text{R}^3$  is a thiol-functional group can be coupled to a fluorinated polyether having at least two epoxy-functional groups.

Examples of preferred silicon compounds are alkoxyalkylsilyl isocyanates, alkoxyalkyl alkyl isocyanates, alkoxy silanes, alkoxyalkyl silanes, and alkoxyalkylsilyl mercapto-, amino-, and glycidyl-functional compounds, such as 3-methyldimethoxy silylpropyl isocyanate, 3-trimethoxy silylpropyl isocyanate,

- 3-triethoxy silylpropyl isocyanate,  
3-mercaptopropyl trimethoxy silane,  
3-mercaptopropyl methyldimethoxy silane,  
3-aminopropyl trimethoxy silane,  
5 3-aminopropyl triethoxy silane, and  
3-glycidoxypentyl trimethoxy silane.

The thus obtained fluorinated resins are also the subject of the present invention.

- 10 In general, good results in both anti/non-fouling properties and mechanical strength are found when the fluorinated resin has a  $T_g$  in the range from -120 to 20°C and a surface energy in the range from 10 to 25 mN/m. In general, mechanical properties improve when the  $T_g$  of the resin is increased, foul release properties improve when the  $T_g$  of the material is lowered. So, for each  
15 fluorinated resin an optimum balance has to be found between mechanical properties and foul release properties by tuning the  $T_g$  of the resin. This tuning can, e.g., be done by varying the length of the  $R^f$  segment or the W segment

- A coating composition can be prepared by mixing the fluorinated resin, a curing  
20 catalyst, for example a condensation catalyst, optionally a co-catalyst, optionally a crosslinker for the resin, a reactive or non-reactive fluid additive, solvents, fillers, pigments and/or thixotropes.

- Examples of catalysts that may be used include the carboxylic acid salts of  
25 various metals, such as tin, zinc, iron, lead, barium, and zirconium. The salts preferably are salts of long-chain carboxylic acids, for example dibutyltin dilaurate, dibutyltin dioctoate, iron stearate, tin (II) octoate, and lead octoate. Further examples of suitable catalysts include organobismuth and organotitanium compounds and organo-phosphates such as 2-ethyl-hexyl  
30 hydrogen phosphate. Other possible catalysts include chelates, for example dibutyltin acetoacetate. Further, the catalyst may comprise a halogenated organic acid, which has at least one halogen substituent on a carbon atom

which is in  $\alpha$ -position relative to the acid group and/or at least one halogen substituent on a carbon atom which is in  $\beta$ -position relative to the acid group, or a derivative which is hydrolysable to form such an acid under the conditions of the condensation reaction.

5

The presence of a cross-linker for the resin is only necessary if the resin cannot be cured by condensation. This depends on the functional groups that are present in the fluorinated resin. In general, when the fluorinated resin comprises alkoxy groups, the presence of a cross-linker is not necessary. If the fluorinated resin comprises alkoxy-silyl groups, in general the presence of a small amount of a condensation catalyst and water is sufficient to achieve full cure of the coating after application. For these compositions, normally atmospheric moisture is sufficient to induce curing and as a rule it will not be necessary to heat the coating composition after application.

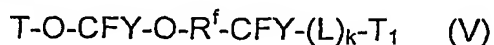
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The crosslinker that is optionally present can be a cross-linking agent comprising a functional silane and/or one or more oxime groups. Examples of such cross-linking agents are presented in WO99/33927. Mixtures of different cross-linkers can also be used.

20

Examples of reactive or non-reactive fluid additives that can be used in the coating composition according to the present invention are non- or monofunctional fluorinated polyethers. These compounds can be represented by the following structure:

25



wherein

- k is an integer 0 or 1,
- T is selected from  $-CF_3$ ,  $-C_2F_5$ ,  $-C_3F_7$ ,  $CF_2Cl$ ,  $C_2F_4Cl$ ,  $C_3F_6Cl$ ,
- $T_1 = -O-T$  when  $k=0$ ,  $T_1=W$  when  $k$  is 1.

30

and wherein  $R^f$ , Y, and L have the meaning as defined before.



Commercial products are available from Ausimont, e.g. Fomblin® Y25. Other unreactive oils such as silicone oil, especially methyl-phenyl silicone oil, petrolatum, polyolefin oil, or a polyaromatic oil can also be used. The proportion of these reactive or non-reactive fluid additives may be in the range of from 0 to 25% by weight, based on the total weight of the coating composition.

Examples of solvents that can be used in the coating composition according to the present invention include polar solvents or mixtures thereof, such as methyl isobutyl ketone or butyl acetate. Non-polar solvents or mixtures thereof, for example xylene, can be used as co-solvents

Examples of fillers that can be used in the coating composition according to the present invention are barium sulphate, calcium sulphate, calcium carbonate, silicas or silicates (such as talc, feldspar, and china clay), aluminium paste/flakes, bentonite or other clays. Some fillers may have a thixotropic effect on the coating composition. The proportion of fillers may be in the range of from 0 to 25% by weight, based on the total weight of the coating composition.

Examples of pigments that can be used in the coating composition according to the present invention are black iron oxide and titanium dioxide. The proportion of pigments may be in the range of from 0 to 10% by weight, based on the total weight of the coating composition.

The coating composition can be applied by normal techniques, such as brush, roller or spray (airless and conventional). To achieve proper adhesion to the substrate it is preferred to apply the anti/non-fouling coating composition to a primed substrate. The primer can be any conventional primer/sealer coating system. Good results were found, in particular with respect to adhesion, when using a primer that comprises an acrylic siloxy-functional polymer, a solvent, a thixotropic agent, filler, and, optionally, a moisture scavenger. Such a primer is disclosed in WO 99/33927.

It is also possible to apply the coating composition in the process according to the present invention on a substrate containing an aged anti-fouling coating layer. Before the coating composition is applied to such an aged layer, this old layer is cleaned by high-pressure water washing to remove any fouling. The  
5 primer disclosed in WO 99/33927 can be used as a tie coat between the aged coating layer and the coating composition according to the present invention.

In general, low-surface energy coatings such as coatings comprising silicones or fluoropolymers do not provide a sound base for application of the coating composition according to the present invention, not even after the application of  
10 a tie-coat, since the adhesion between the aged coating layer and the freshly applied coating layer in general is insufficient.

After the coating has been cured, it can be immersed immediately and gives immediate anti-fouling and fouling release protection.

15

As indicated above, the coating composition used in the process according to the present invention has very good anti-fouling and foul release properties in combination with a high mechanical strength. This makes these coating compositions very suitable for use as anti-fouling or non-fouling coatings for  
20 marine applications. The coating can be used for both dynamic and static structures, such as boat hulls, buoys, drilling platforms, oil production rigs, and pipes which are immersed in water. The coating can be applied on any substrate that is used for these structures, such as metal, concrete, wood or fibre-reinforced resin.

25

The coating compositions used in the process according to the present invention are preferably applied as high solids formulations. These compositions comprise less than 30% by weight of solvent, preferably less than 20%, still more preferably less than 10%. These formulations belong to the  
30 class of solventless coatings. Such coatings have minimal environmental impact in view of their low solvent content.

The combination of low (ambient) temperature curing of the resins and high solids content of the coating composition makes the coating compositions according to the present invention suitable for application in the open field.

- 5 The invention will be elucidated with reference to the following examples. These are intended to illustrate the invention, but are not to be construed as limiting in any manner the scope thereof.

## Examples

### Example 1

- 5 Preparation of an adduct of a perfluoroether
- 200 pbw of a bifunctional perfluoropolyether of formula (II) having  $n=0$  and a number average molecular weight of 1000 were added to a flange-topped reaction vessel with a mechanical stirrer, a temperature probe, a water condenser, and a feed inlet. After the addition of 0,02 pbw of dibutyltin dilaurate
- 10 (DBTDL), the reaction vessel was heated to 70°C. At this temperature, 88 pbw of 3-(trimethoxysilylpropyl)isocyanate (TMSPI) were added dropwise over a two-hour period. During the addition the temperature was maintained at 70°C using a temperature control unit. After the completion of the feed, the solution was stirred for another hour to complete the reaction. The progress of the
- 15 reaction could be monitored by measuring the decrease of the infrared absorption of TMSPI at  $\sim 2270\text{cm}^{-1}$ .

The adduct has a viscosity at 25°C of 4,1 Poise (0,41 Pa.s) and a  $T_g$  of -26°C.

### Example 2

- 20 Preparation of an adduct of an ethoxylated perfluoroether
- Using the same process as described in Example 1, a bifunctional perfluoropolyether of formula (II) having  $n=1,5$  and a number average molecular weight of 2000 was used as a perfluoroether starting component in the reaction.
- 25 The formed adduct has a viscosity at 25°C of 8,1 Poise (0,81 Pa.s) and a  $T_g$  of -97°C.

### Example 3

- Using the process of Example 1, a perfluorinated adduct was obtained by a
- 30 reaction between a bifunctional diester of formula (III) wherein  $R=\text{CH}_3$  having a number average molecular weight of 2000 and an equimolar amount of 3-

aminopropyl trimethoxysilane at 70°C. During the reaction methanol was removed by distillation until the ester IR-band at about 1800 cm<sup>-1</sup> had disappeared completely.

5    Example 4

A one-pack coating composition was prepared by combining

- 100 g of the adduct of a perfluoroether of Example 1
- 10 g of butyl acetate
- 0,2 g of 3-aminopropyl trimethoxy silane
- 10    0,1 g of dibutyltin dilaurate

After application of this coating composition on a wooden substrate and curing of the composition, a coating was obtained with a modulus at 20°C of 42,5 Mpa (measured in accordance with ASTM D1708) and a pencil hardness of 3H (measured in accordance with ASTM D3363)

15

Example 5

A one-pack coating composition was prepared by combining

- 100 g of the adduct of a perfluoroether of Example 1
- 20 g of butyl acetate
- 20    0,2 g of 3-aminopropyl trimethoxy silane
- 0,1 g of dibutyltin dilaurate
- 3 g of Fomblin Y-25 (a perfluorinated polyether, ex Ausimont)

Example 6

25    A two-pack coating composition was prepared by having

100 g of the adduct of a perfluoroether of Example 2

in one pack and combining

- 10 g of butyl acetate
- 0,2 g of 3-aminopropyl trimethoxy silane
- 30    0,1 g of dibutyltin dilaurate

in the other pack.

After application of this coating composition on a wooden substrate and curing of the composition, a coating was obtained with a modulus at 20°C of 3,1 Mpa (measured in accordance with ASTM D1708) and a pencil hardness of 4B

35    (measured in accordance with ASTM D3363)

Example 7

A one-pack coating composition was prepared by combining

- 100 g of the adduct of a perfluoroether of Example 1
- 5 10 g of butyl acetate
- 0,2 g of 3-aminopropyl trimethoxy silane
- 0,1 g of dibutyltin dilaurate
- 30 g of talc
- 6 g of black iron oxide
- 10 25 g of aluminium flake

Example 8

A one-pack coating composition was prepared by combining

- 100 g of the adduct of a perfluoroether of Example 2
- 15 20 g of butyl acetate
- 1 g of 2-ethylhexylhydrogen phosphate
- 3 g of Fomblin Y-25 (a perfluorinated polyether, ex Ausimont)

The coating compositions of Examples 4 - 8 were applied to wood substrates bearing an anti-corrosive undercoat and coating primers as disclosed in WO 99/33927. The coating formulations were applied by brush and roller to give a layer of average dry film thickness in the range from 25 to 75  $\mu\text{m}$ .

For static anti-fouling assessment the coated substrates were immersed in a marine estuary known for its weed, slime, hard-shelled and soft-bodied animal fouling. After one season (February - October) the accumulated fouling was significantly less than that of control substrates not coated with the compositions and maintained under the same conditions over the same period of time. Any fouling on the substrates with the compositions of Examples 4 - 8 could be removed easily by light rubbing or low-pressure water jet. Accumulated fouling on the control substrates immersed over the same period could not be removed in a similar way.

For these coating compositions the following quantitative fouling properties were found:

Example	% micro fouling	% soft-bodied animal	% hard-bodied animal	% total fouling	Push-off (PSI)*
4	25	1.7	56.7	83.4	20.55
5	23.8	3.5	41.3	68.6	11.04
6	28.8	2.2	50	81	13.34
7	19.7	2.2	6.8	28.7	6.24
8	51.4	4.2	22.4	78	9.11

\*) Measured in accordance with ASTM standard D-5618, barnacle type *Semibalanus Balanoides*

#### Example 9

- 5 A coating composition was prepared by combining
- 100 g of the adduct of a perfluoroether of Example 3
  - 20 g of butyl acetate
  - 1 g of 2-ethylhexylhydrogen phosphate
  - 3 g of Fomblin Y-04 (a perfluorinated polyether, ex Ausimont)

10

#### Example 10

A coating composition was prepared by combining

- 100 g of the adduct of a perfluoroether of Example 2
- 20 g of butyl acetate
- 15 g of titaniumdioxide
- 1 g of 2-ethylhexylhydrogen phosphate
- 6 g of Fomblin Y-25 (a perfluorinated polyether, ex Ausimont)

15

The coating compositions of Examples 9 and 10 were applied to wood  
20 substrates bearing an anti-corrosive undercoat and coating primers as disclosed in WO 99/33927. The coating formulations were applied by brush and roller to give a layer of average dry film thickness in the range from 25 to 75 µm.

For static anti-fouling assessment the coated substrates were immersed in a  
25 marine estuary known for its weed, slime, hard-shelled and soft-bodied animal fouling.

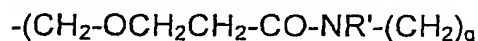
## Claims

1. A process for inhibiting the fouling of a substrate in a marine fouling environment, which comprises forming on the substrate, before exposure to the said environment, a coating comprising a curable fluorinated resin of the general formula:
- W - L - YFC - O - R<sup>f</sup> - CFY - L - W
- wherein
- L is an organic linking group;
  - Y is F or CF<sub>3</sub>;
  - W is a group of general formula -Si(R<sup>1</sup>)<sub>α</sub>(OR<sup>2</sup>)<sub>3-α</sub>, wherein α = 0, 1, or 2, R<sup>1</sup> and R<sup>2</sup> independently have the meaning of linear or branched C1-C6 alkyl groups, optionally containing one or more ether groups, or C7-C12 aryl or alkyl groups;
  - R<sup>f</sup> is a group having an average molecular weight by number between 350 and 8000, comprising repeating units having at least one of the following structures randomly distributed along the chain:  
 -CFXO-, -CF<sub>2</sub>CF<sub>2</sub>O-, -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-, -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-,  
 -CR<sup>4</sup>R<sup>5</sup>CF<sub>2</sub>CF<sub>2</sub>O-, -(CF(CF<sub>3</sub>)CF<sub>2</sub>O)-, -CF<sub>2</sub>CF(CF<sub>3</sub>)O-,
- wherein
- X is F or CF<sub>3</sub>,
  - R<sup>4</sup> and R<sup>5</sup> independently have the meaning of H, Cl, or C1-C4 perfluoroalkyl.
2. A process according to claim 1, characterised in that the organic linking group L is selected from one or more of the following groups:
- a) -(CH<sub>2</sub>-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>)<sub>m</sub>-CO-NR'-(CH<sub>2</sub>)<sub>q</sub>,
  - b) -CH<sub>2</sub>O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-
  - c) -CH<sub>2</sub>O-CH<sub>2</sub>-CH(OH)CH<sub>2</sub>-S-(CH<sub>2</sub>)<sub>q</sub>
- wherein
- R' is H, C<sub>1</sub>-C<sub>4</sub> alkyl or a phenyl group;



- m is an integer equal to 0 or 1;
- n is an integer in the range 0-8;
- q is an integer in the range 1-8;

5 3. A process according to claim 2, characterised in that the organic linking group L has the formula



wherein n is an integer in the range 0-5 and q is an integer in the range 1-3.

10 4. A process according to any one of the preceding claims, characterised in that R<sup>f</sup> is selected from one or more of the following groups:

1)  $-(\text{CF}_2\text{O})_a-(\text{C}_2\text{F}_4\text{O})_{b'-}$ , wherein a'/b' is between 0,2 and 2, a' and b' being integers giving a molecular weight in the range from 350 to 8000;

15 2)  $-(\text{C}_3\text{F}_6\text{O})_r-(\text{C}_2\text{F}_4\text{O})_b-(\text{CFXO})_{t'-}$ , wherein r/b is between 0,5 and 2 and (r+b)/t is between 10 and 30, b, r, and t being integers giving a molecular weight in the range from 350 to 8000;

3)  $-(\text{C}_3\text{F}_6\text{O})_{r'}-(\text{CFXO})_{t'}-\text{CF}_2(\text{R}'^f)_y-\text{CF}_2\text{O}-(\text{CFXO})_{t'}-(\text{C}_3\text{F}_6\text{O})_{r'-}$ , wherein t' is larger than 0, r'/t' is between 10 and 30, r' and t' being integers giving a molecular weight in the range from 350 to 8000, y is 0 or 1, and R<sup>f</sup> is a C1-C4 fluoroalkyl group.;

20

4)  $-(\text{C}_3\text{F}_6\text{O})_z-\text{CF}_2-(\text{R}'^f)_y-\text{CF}_2\text{O}-(\text{C}_3\text{F}_6\text{O})_{z'-}$ , wherein z is an integer giving a molecular weight in the range from 350 to 8000, y is 0 or 1, and R<sup>f</sup> is a C1-C4 fluoroalkyl group;

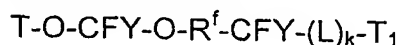
25 5)  $-(\text{OCF}_2\text{CF}_2\text{CR}^4\text{R}^5)_q-\text{OCF}_2-(\text{R}'^f)_y-\text{CF}_2\text{O}-(\text{CR}^4\text{R}^5\text{CF}_2\text{CF}_2\text{O})_{s'-}$ , wherein q and s are integers giving a molecular weight in the range from 350 to 8000, R<sup>4</sup> and R<sup>5</sup> have the meaning given above, y is 0 or 1, and R<sup>f</sup> is a C1-C4 fluoroalkyl group;

whereby in the above structures  $-(\text{C}_3\text{F}_6\text{O})-$  can be  $-(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})-$  or  $-(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})-$ .

30

5. A process according to any one of the preceding claims, characterised in that the fluorinated resin has a  $T_g$  in the range from  $-120$  to  $20^\circ\text{C}$  and a surface energy in the range from 10 to 25 mN/m.

5 6. A process according to any one of the preceding claims, characterised in that it further comprises a non-functional or mono-functional resin of the general formula:



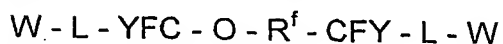
wherein

- 10 - k is an integer 0 or 1;
- T is selected from  $-\text{CF}_3$ ,  $-\text{C}_2\text{F}_5$ ,  $-\text{C}_3\text{F}_7$ ,  $\text{CF}_2\text{Cl}$ ,  $\text{C}_2\text{F}_4\text{Cl}$ ,  $\text{C}_3\text{F}_6\text{Cl}$ ;
- $\text{T}_1 = -\text{O-T}$  when  $k=0$ ,  $\text{T}_1=\text{W}$  when  $k$  is 1;
- L is an organic linking group;
- Y is F or  $\text{CF}_3$ ; and
- 15 -  $\text{R}^f$  is a group having an average molecular weight by number between 350 and 8000, comprising repeating units having at least one of the following structures randomly distributed along the chain:  
 $-\text{CFXO}-$ ,  $-\text{CF}_2\text{CF}_2\text{O}-$ ,  $-\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$ ,  $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$ ,  
 $\text{CR}^4\text{R}^5\text{CF}_2\text{CF}_2\text{O}-$ ,  $-(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})-$ ,  $-\text{CF}_2\text{CF}(\text{CF}_3)\text{O}-$ ,

20 wherein

- X is F or  $\text{CF}_3$ ;
- $\text{R}^4$  and  $\text{R}^5$  independently have the meaning of H, Cl, or C1-C4 perfluoroalkyl.

25 7. Use of a curable fluorinated resin of the general formula:



wherein

- L is an organic linking group;
- Y is F or  $\text{CF}_3$ ;
- 30 - W is a group of general formula  $-\text{Si}(\text{R}^1)_\alpha(\text{OR}^2)_{3-\alpha}$ , wherein  $\alpha = 0, 1, \text{ or } 2$ ,  $\text{R}^1$  and  $\text{R}^2$  independently have the meaning of linear or branched C1-C6

alkyl groups, optionally containing one or more ether groups, or C7-C12 aryl or alkyl groups;

-  $R^f$  is a group having an average molecular weight by number between 350 and 8000, comprising repeating units having at least one of the following structures randomly distributed along the chain:

-CFXO-, -CF<sub>2</sub>CF<sub>2</sub>O-, -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-, -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-,  
CR<sup>4</sup>R<sup>5</sup>CF<sub>2</sub>CF<sub>2</sub>O-, -(CF(CF<sub>3</sub>)CF<sub>2</sub>O)-, -CF<sub>2</sub>CF(CF<sub>3</sub>)O-,

wherein

- X is F or CF<sub>3</sub>,

- R<sup>4</sup> and R<sup>5</sup> independently have the meaning of H, Cl, or C1-C4 perfluoroalkyl,

in antifouling or non-fouling coating compositions for marine use.

8. Use according to claim 7, characterised in that the fluorinated resin has a T<sub>g</sub> in the range from -120 to 20°C and a surface energy in the range from 10 to 25 mN/m.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/06359

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G65/00 C09D171/02 C09D5/16 C08G65/32

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 37720 A (MINNESOTA MINING & MFG) 29 July 1999 (1999-07-29) claim 1 tables 1,2	1-8
A	EP 0 433 070 A (MINNESOTA MINING & MFG) 19 June 1991 (1991-06-19) example 1	1-8
A	US 4 614 667 A (LARSON JAMES M ET AL) 30 September 1986 (1986-09-30) * structure XV *	1-8
A	EP 0 731 125 A (AUSIMONT SPA) 11 September 1996 (1996-09-11) example 8	1-8
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/06359

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 770 634 A (OCE NEDERLAND BV) 2 May 1997 (1997-05-02) claims 1,5 ---	1-9
A	DATABASE WPI Section Ch, Week 199247 Derwent Publications Ltd., London, GB; Class A26, AN 1992-385322 XP002155368 & JP 04 283248 A (TOSHIBA SILICONE KK), 8 October 1992 (1992-10-08) abstract ---	1-8
A	EP 0 251 334 A (MONTEDISON SPA) 7 January 1988 (1988-01-07) claim 1 page 2, line 17 - line 22 -----	1-8

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/06359

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9937720	A	29-07-1999	US 6277485 B1 AU 7959398 A CN 1284105 T EP 1051448 A1 WO 9937720 A1	21-08-2001 09-08-1999 14-02-2001 15-11-2000 29-07-1999
EP 0433070	A	19-06-1991	AU 632869 B2 AU 6669890 A BR 9006319 A CA 2030221 A1 DE 69025151 D1 DE 69025151 T2 EP 0433070 A2 ES 2081949 T3 JP 3009744 B2 JP 3258863 A KR 178513 B1 US 5306758 A	14-01-1993 20-06-1991 24-09-1991 15-06-1991 14-03-1996 19-09-1996 19-06-1991 16-03-1996 14-02-2000 19-11-1991 01-04-1999 26-04-1994
US 4614667	A	30-09-1986	US 4567073 A	28-01-1986
EP 0731125	A	11-09-1996	IT MI950474 A1 AT 202790 T AU 699409 B2 AU 4794696 A CA 2171229 A1 DE 69613610 D1 EP 0731125 A1 ES 2158965 T3 JP 8259882 A US 5959058 A ZA 9601922 A	10-09-1996 15-07-2001 03-12-1998 19-09-1996 11-09-1996 09-08-2001 11-09-1996 16-09-2001 08-10-1996 28-09-1999 12-09-1996
EP 0770634	A	02-05-1997	NL 1001472 C2 NL 1001471 C2 DE 69609288 D1 DE 69609288 T2 EP 0770634 A2 EP 0773482 A1 JP 2873214 B2 JP 9138594 A JP 3150290 B2 JP 9151235 A US 5677406 A US 5742889 A	25-04-1997 25-04-1997 17-08-2000 18-01-2001 02-05-1997 14-05-1997 24-03-1999 27-05-1997 26-03-2001 10-06-1997 14-10-1997 21-04-1998
JP 4283248	A	08-10-1992	NONE	
EP 0251334	A	07-01-1988	IT 1213449 B AU 592653 B2 AU 7501887 A CA 1318445 A1 DE 3774006 D1 DK 339787 A EP 0251334 A1 ES 2027262 T3 JP 2617313 B2 JP 63092631 A	20-12-1989 18-01-1990 07-01-1988 25-05-1993 28-11-1991 04-01-1988 07-01-1988 01-06-1992 04-06-1997 23-04-1988

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/06359

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0251334	A	NO 872774 A ,B, PT 85219 A ,B US 4851475 A ZA 8704691 A	04-01-1988 01-07-1987 25-07-1989 27-04-1988
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